Corrosion Science 80 (2014) 139–142

Contents lists available at ScienceDirect

Corrosion Science

journal homepage: www.elsevier.com/locate/corsci

Effect of prior deformation and heat treatment on the corrosion-induced hydrogen trapping in aluminium alloy 2024

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ARTICLE INFO

Article history:
Received 13 August 2013
Accepted 17 November 2013
Available online 24 November 2013

Keywords:
A. Aluminium
C. Exfoliation corrosion
C. Effects of strain
C. Hydrogen absorption

ABSTRACT

The nature of the corrosion-induced hydrogen trapping in Al-alloy 2024-T351 was studied by thermal desorption spectroscopy. The microstructure was altered by solution treatment and plastic deformation, prior to corrosion. The results showed that the high temperature, 500 °C, trap state (T4 state) is associated with the S-phase. In the absence of S-phase, hydrogen is trapped at vacancies, which liberate hydrogen at higher temperatures. Plastic deformation prior to corrosion revealed that the trap state at 400 °C (T3 state) is associated with dislocations. High plastic strains (above 0.06) lead to a reduction of hydrogen trapped in both dislocations and the S-phase.

1. Introduction

Hydrogen evolution during environmental or corrosion exposure and subsequent trapping in the microstructure, has been linked to the embrittlement of aluminium alloy 2024 [1]. In order to investigate hydrogen embrittlement, a wide variety of methods to introduce hydrogen have been used over the years, such as cathodic charging, exposure to humid air as well as exposure to a corrosive environment. Hydrogen is produced during the corrosion process by surface corrosion reactions and part of it diffuses towards the interior of the material, where it may be retained at various preferential locations described as traps by Pressouyre [2]. These traps can be thermally activated and liberate hydrogen at different temperatures. Hydrogen traps are classified as reversible and irreversible, depending on the steepness of the energy barrier, the hydrogen has to overcome in order to be liberated.

An accurate method for studying hydrogen evolution is thermal desorption spectroscopy (TDS). This technique has been successfully applied to the studies of hydrogen trapping in various materials with BCC and FCC structure [1,3–5] e.g. in nickel [3,6], pure aluminium [7], Al–Cu, Al–Mg_2Si [8], Al–Li alloys [9,10], Al–Li–Cu–Zr [11] as well as pure iron and steel [12–14]. A wide variety of TDS measurements combined with metallurgical experiments, like heat treatments for second-phase particle precipitation or dissolution, as well as cold working for dislocation multiplication have been conducted over the years in order to investigate the nature of trapping sites in nickel, steel, pure aluminium as well as Al alloys [5,8,15–17].

Hydrogen uptake and trap binding energy were determined by Ai et al. [18] for Monel K-500 in several conditions (single-phase solid solution, aged, and cold worked and aged microstructures), using TDS. Their results suggested hydrogen trapping at incoherent γ' (Ni_3Al) precipitates. Lee and Lee [16] investigated the trapping and transport phenomena of hydrogen in nickel. They reached the conclusion that dislocations in nickel act as trapping sites of hydrogen, and the hydrogen trap activation energy at dislocations appears to be lower than the activation energy for the bulk diffusion of hydrogen. It was suggested that both hydrogen trapping at grain boundaries and short-circuit diffusion through grain boundaries in nickel are present. The impact of grain size on hydrogen diffusion and trapping mechanisms has been investigated for a wide range of grain sizes in nontextured pure nickel by Oudriss et al. [3]. Their results suggested that hydrogen diffusion is accelerated along the boundaries but may slow down when the dislocation density stored in the boundary becomes substantial [3,6].

Young and Scully [5] performed TDS in pure aluminium. The desorption spectra revealed three distinct trapping states. The lowest energy peak was attributed to hydrogen occupying interstitial lattice sites. The intermediate peak around 400 °C was associated with hydrogen trapped at dislocations, while the 500 °C trap state with vacancies. Izumi and Itoh [7], investigated hydrogen trapping states in pure aluminium foils with 99.99% purity with different amount of blisters by means of TDS. Blisters as well as vacancies have been identified as potential hydrogen trapping sites. More specifically in aluminium alloys, it has been shown [8,19] that lattice defects (vacancies, dislocations, grain boundaries, subgrain

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0010-938X/$ - see front matter © 2013 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.corsci.2013.11.021

boundaries, interfaces), second-phase particles and precipitates provide a variety of trapping sites. Saitoh et al. [8] and Iijima et al. [20] have used tritium microautoradiography to investigate hydrogen trapping in high purity aluminium, Al–4Cu, Al–Mg_2Si, and an Al–6Zn–2Mg (wt%) alloy. Their work showed that, in general, microstructural features possessing a tensile stress field act as hydrogen traps while features with a compressive stress field act as hydrogen repellers. In some alloys, trapping was observed at dislocations introduced by cold work and at interfacial dislocations associated with tensile elastic stress fields El-Amoush [21] investigated the effect of hydrogen on the hardness of 7075-T6 aluminium alloy. It was shown that the introduction of hydrogen caused hardening on the surface of 7075-T6 aluminium alloy. Further charging increased the depth of the hardened region. Transmission electron microscopic observations of the hardened hydrogen-enriched layer revealed an increase in dislocation density. Aging after charging resulted in either complete or partial recovery of hardness depending on the charging conditions applied to the material.

Previous work concerning corrosion-induced hydrogen uptake and trapping in alloy 2024, have shown four operational hydrogen trapping states (T1–T4) [22]. Trap T1 was considered to be a reversible trap, which liberates hydrogen continuously at low temperatures. Traps T2, T3 and T4 saturate with exposure time and were considered to be irreversible, with critical hydrogen evolution temperatures of 200, 410 and 500 °C respectively. However, a detailed understanding of this behaviour pattern has not been achieved. The present investigation has been conducted in an attempt to gain a better insight of hydrogen trapping in aluminium alloy 2024. To that end the experiments were designed to alter the materials microstructure prior to corrosion exposure and associated hydrogen uptake. In the first set of experiments the material was solution treated and quenched (condition SQ) prior to corrosion exposure. This condition is compared with the standard solution treated, quenched and aged condition (SQA) in order to reveal the effect of the S-phase (Al_2CuMg) on hydrogen trapping. In the second set of experiments, the material was plastically deformed at certain levels of plastic strain prior to corrosion exposure, in order to reveal the effect of plastic deformation on hydrogen trapping.

2. Materials and methods

The material used for the present study was alloy 2024-T351, supplied by Airbus with thickness of 3 mm. The chemical composition of the alloy is Al–4.35Cu–1.5 Mg–0.64Mn–0.5Si–0.5Fe (wt%). Specimens with dimensions 3 × 3 × 25 mm were cut from the alloy sheet. Exfoliation corrosion testing (EXCO) was performed according to ASTM specification G34-90. It included exposure at 25 ± 0.5 °C, in a solution containing 234 g NaCl, 50 g KNO_3 and 6,3 ml concentrated HNO_3 (70 wt%) diluted to 1 L of distilled water. Specimen cleaning after removal from the corrosive solution involved soaking in concentrated HNO_3 for 5 min, rinsing in water, then in acetone and thorough drying in a purge of warm air. The cleaning process aimed at the complete removal of corrosion products and its duration did not exceed 10 min. The above conditions were identical for all specimens exposed to the corrosive solution. The surface area of each specimen was 318 mm^2.

An in-house thermal desorption spectroscopy/gas chromatography system (TDS) was employed in order to determine hydrogen being trapped in the alloy during corrosion. The corroded specimens were introduced in a thermostated furnace and held under continuous nitrogen flow. A constant heating rate of 10 °C/min was applied, and the amount of hydrogen evolved was measured as a function of specimen temperature. Heating was performed up to 600 °C and then the temperature was kept constant at 600 °C until all hydrogen was degassed.

For the first experiment the specimens were first solution-treated at 490 °C for 30 min and then quenched in cold water. This series was termed SQ (solution treated and quenched only). The specimens were not allowed to naturally age, but instead they were exposed to the EXCO solution for 6 and 12 h. The time between the water quench and the start of the corrosion process did not exceed 10 min in all cases. The reason for selecting short exposure times was to avoid hydrogen trapping from precipitates that could form during the corrosion exposure period. The times of 6 and 12 h are short compared to the 3 day period employed for natural aging of the alloy. Another series of specimens were solution treated at 490 °C for 30 min, followed by quench in cold water and were subsequently naturally aged at room temperature for 3 days. This series was termed SQA (solution, quenched & aged). The specimens were then exposed to the EXCO solution for 6 and 12 h. TDS measurements were performed immediately after removing the corrosion products from both the SQ and SQA series. The time between corrosion testing and TDS measurements did not exceed 10 min in all cases.

The second experiment involved plastic deformation prior to corrosion exposure. Tensile specimens were prepared according to the ASTM specification E8m-94a. The specimens were subjected to tensile testing at room temperature at a constant strain rate of $6 \times 10^{-4}\ s^{-1}$. The tests were interrupted at specified levels of strain (0.015, 0.045, 0.06, 0.1, 0.12, 0.14 and 0.15). After tensile testing, strips 3 mm wide and 25 mm long were cut from the gage section (two strips per tensile specimen). Surface material was removed from all sides by grinding with 1000 grit paper, in order is to ensure a clean and smooth surface. Finally they were rinsed in acetone, dried and exposed for 24 h in the exfoliation corrosion solution. After removal from the corrosive solution they were cleaned, rinsed in distilled water and acetone and dried in warm air. TDS spectra were taken immediately after cleaning.

3. Results and discussion

The desorption spectrum for both the SQ and SQA series is shown in Fig. 1. It should be noted that the spectrum is divided in two parts. The first part corresponds to the ramped spectrum where the temperature is increasing at a constant rate (10 °C/min) while the second part corresponds to isothermal holding

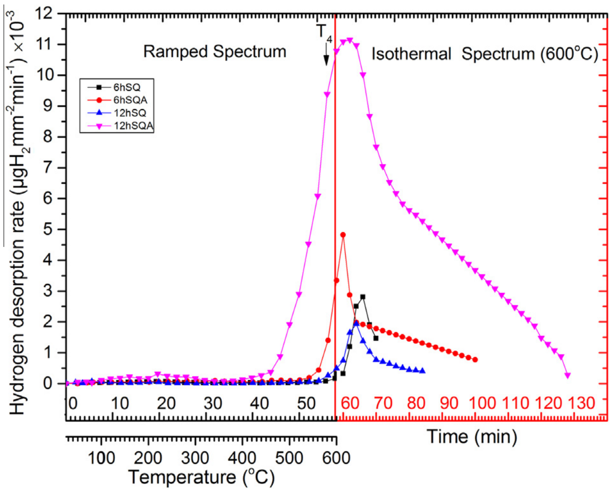

Fig. 1. Spectrum of hydrogen evolved from the solution treated and quenched (SQ) as well as solution treated quenched and aged (SQA) specimens after 6 and 12 h in the EXCO solution.